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INCREASING THE SOLUBILITY OF INERT PERIPHERALLY AROMATIC POSS

Brian M. Moore,¹ Sean M. Ramirez,² Gregory R. Yandek,¹ Timothy S. Haddad,² and Joseph M. Mabry¹

¹Air Force Research Laboratory, Space & Missile Propulsion Division, Edwards Air Force Base, CA 93524-7680

²ERC Inc., Air Force Research Laboratory, Space & Missile Propulsion Division, Edwards Air Force Base, CA 93524-7680

Abstract

New POSS compounds with high temperature capability and good solubility in various organic solvents have been developed. By placing a single polycyclic aromatic group (naphthyl, phenanthryl, or pyrenyl) on a corner (via a "corner-capping" reaction) of (phenyl)₃Si₇O₉(OH)₃, cage symmetry is disrupted, which significantly increases solubility over (phenyl)₈Si₈O₁₂. Thermal characteristics are retained, which makes these materials suitable for use in high performance polymers. Reasonable yields (29-95%) were obtained for the reactions.

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¹Air Force Research Laboratory, Space & Missile Propulsion Division, Edwards Air Force Base, CA 93524-7680

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Introduction

Polyhedral Oligomeric Silsesquioxanes (POSS) combine an inorganic Si-O core surrounded by eight substituent groups that form an organic corona. These hybrid nanoparticles are used in many applications due to their solubility in solvent and polymer hosts.¹ The versatility of POSS chemistry affords various forms of organic functionality, each having strengths and weaknesses, which may be tailored for a particular application. For instance, aliphatic groups tend to have good solubility in a number of materials but demonstrate poor thermal properties. Fluorinated groups impart low surface energy, but have low solubility in common organic solvents.² Peripherally aromatic POSS, on the other hand, are thermally stable, but suffer from poor solubility.³⁻⁴ Commercially available inert aromatic POSS compounds are phenyl₈Si₈O₁₂ and phenyl₁₂Si₁₂O₁₈. The symmetry, low dipole moments, and high degree of aromaticity of these compounds all contribute to significant micro-scale crystallinity resulting in extraordinarily poor solubility in hosts, including those that are chemically similar. The POSS interactions within these crystals are considerably strong such that they do not exhibit melting points and cannot be mechanically broken. In an effort to improve solubility, the physical peripheral structure of POSS has been modified using a "corner-capping" methodology. By placing a single polycyclic aromatic group (naphthyl, phenanthryl, or pyrenyl), on one corner of an octa-functional cage, improved solubility characteristics are observed. Replacement of a single phenyl group with a larger aromatic moiety disrupts the cage symmetry thus solubility is substantially increased, yet does not compromise the superb thermal properties characteristic of this class of compounds. This molecular architecture represents a new class of non-reactive, blendable nanoparticles for the thermal and mechanical reinforcement of polymer hosts.

Experimental

Materials. Phenyl₈ POSS trisilanol was obtained from Hybrid Plastics, while other silicon-containing organic compounds were purchased from Gelest. All other chemicals were purchased from Aldrich. All chemicals were used without further purification unless noted otherwise. All reactions were performed under an atmosphere of dry nitrogen. Flasks were oven-dried and allowed to cool under nitrogen prior to use.

Instrumentation. ¹H, ¹³C, and ²⁹Si NMR spectra were obtained on Bruker 300-MHz and 400-MHz spectrometers using 5 mm o.d. tubes. Sample concentrations were approx. 10% (w/v) in CDCl₃ and were referenced to internal solvent. ¹H spectra were run with the following delay times to ensure accurate integrals. A 15 sec delay was used to acquire ²⁹Si NMR spectra.

Synthesis of 1-naphthyltrichlorosilane. Under a dry nitrogen atmosphere, a solution of 1-bromonaphthalene (27.7 g, 0.134 mol) in THF (175 mL) was added slowly to a suspension of magnesium turnings (3.9 g, 0.16 mol) in THF (15 mL) that had previously been activated with an iodine crystal. After cooling to room temperature, the Grignard reagent was added via canula to a THF solution of SiCl₄ (25.1 g, 0.148 mol) and stirred overnight. The mixture was evaporated to dryness, extracted with hexane, and filtered to remove MgBrCl. The hexane-soluble 1-naphthyltrichlorosilane was distilled at 120 °C under dynamic vacuum to provide a 67% yield (23.6 g, 0.0902 mol) of product. ¹H NMR (CDCl₃, ppm) 8.46 (dd, ³J_{H-H} 0.7, 8.4 Hz, 1H), 8.21 (dd, ³J_{H-H} 1.2, 7.0 Hz, 1H), 8.09 (d, ³J_{H-H} 8.3 Hz, 1H), 7.96 (d, ³J_{H-H} 7.5 Hz, 1H), 7.70 (m, 1H), 7.59 (m, 2H). ¹³C{¹H} NMR (CDCl₃, ppm) 124.61, 126.53, 127.12, 127.41, 127.88, 129.34, 133.55, 134.04, 134.38, and 135.47. ²⁹Si{¹H} (CDCl₃, ppm) -0.50 (s).

Synthesis of Phenyl-1-naphthylSi₈O₁₂ (1-C₁₀H₇)(C₆H₅)₇Si₈O₁₂. Under a dry nitrogen atmosphere, (C₆H₅)₇Si₇O₉(OH)₃ (19.7 g, 0.021 mol) was dissolved in THF (150 mL). 1-Naphthyltrichlorosilane (5.6 g, 0.022 mol) was dissolved in THF (50 mL) and slowly added to the phenyl triol solution. Triethylamine (6.8 g, 0.068 mol) was diluted with THF (100 mL) and added over a 90 minute period to the stirring solution and the reaction was allowed

to proceed overnight. The solution was then filtered and the volume reduced under dynamic vacuum. Ether was then added and an aqueous workup was performed. The solution was again reduced under vacuum and the remaining oil was dissolved in THF. The solution was precipitated in methanol and then filtered to produce a 95% yield (21.0 g, 0.20 mol). ¹H NMR (CDCl₃, ppm) 8.51 (m, 1H), 8.04 (dd, ³J_{H-H} 1.3, 6.8 Hz, 1H), 7.98 (d, ³J_{H-H} 8.3 Hz, 1H), 7.81 (m, 15H), 7.36 (m, 24H). ¹³C{¹H} NMR (CDCl₃, ppm) 124.84, 125.73, 126.50, 127.85, 127.88, 127.90, 128.26, 128.36, 128.64, 130.05, 130.15, 130.19, 130.77, 130.82, 131.50, 133.16, 134.19, 134.22, 134.23, 135.36, and 136.45. ²⁹Si{¹H} (CDCl₃, ppm) -77.37, -78.05, -78.14, and -78.17. Elemental Anal. (Calcd): C, 57.68 (57.64); H, 3.81 (3.91).

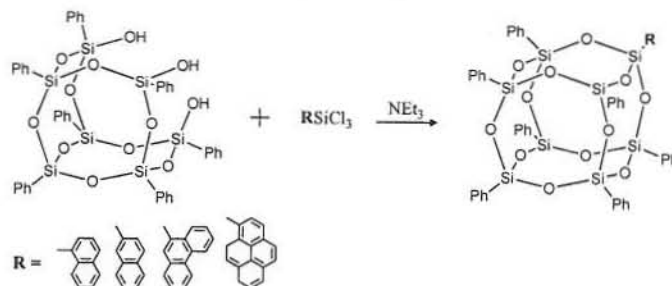


Figure 1. Synthesis for corner-capped POSS cages.

Results and Discussion

Polycyclic aromatic (phenyl)₇Si₈O₁₂ cages were produced using a similar method as found in the literature.⁵ The corner capping reactions all had reasonable yields (29-95%) and were easily purified by dissolving in a good solvent and then slowly adding to a poor solvent.

The substitution of one aromatic group on the POSS cage exerts significant effects on miscibility characteristics. The solubility in chloroform, as compared to octaphenyl POSS, increased by more than an order of magnitude. Octaphenyl POSS is insoluble in common organic solvents, whereas the polyaromatic corner capped POSS is soluble in several common organic solvents. This opens up several possibilities for incorporating a high temperature POSS into polymer systems.

Two solutions were made, one consisting of polystyrene and octaphenyl POSS in THF and the other consisting of polystyrene and 1-Nap(Ph)₇T₈ in THF. These polymer solutions were used to solution-cast films onto glass substrates. The films were dried in a vacuum oven slightly above the T_g of the host polymer. The octaphenyl POSS films exhibited micro-phase separation, resulting in a cloudy film. The 1-Nap(Ph)₇T₈ remained dispersed in the polymer system and was optically clear.

Conclusions

New POSS compounds with high temperature capability and good solubility in various organic solvents have been developed at AFRL. By replacing one of the phenyl groups on the cage, symmetry is disrupted, which results in increased solubility. The newly replaced group is also aromatic, so thermal characteristics are retained. These soluble materials are able to be dispersed into high performance polymers, in contrast to their similar commercially available counterparts.

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References

1. Baney, R. H.; Itoh, M.; Sakakibara, A.; Suzuki, T., Silsesquioxanes. *Chem. Rev.* **1995**, *95* (5), 1409.
2. Mabry, J. M.; Vij, A.; Iacono, S. T.; Viers, B. D., Fluorinated polyhedral oligomeric silsesquioxanes (F-POSS). *Angew. Chem., Int. Ed.* **2008**, *47*, 4137.
3. Olsson, K.; Gronwall, C., On Octa-(arylsilsesquioxanes), (ArSi)₈O₁₂. *Ark. Kemi* **1960**, *28*, 529-4.
4. Brown, J. F.; Vogt, L. H.; Prescott, P. I., Preparation and Characterization of the Lower Equilibrated Phenylsilsesquioxanes. *J. Am. Chem. Soc.* **1964**, *86* (6), 1120.
5. Haddad, T. S.; Viers, B. D.; Phillips, S. H., Polyhedral Oligomeric Silsesquioxane (POSS)-Styrene Macromers. *J. Inorg. Organomet. Polym. Mater.* **2001**, *11* (3), 155.